REPLACEMENT OF CHARCOAL SORBENT IN THE VOST

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ABSTRACT

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EPA Method 0030, (VOST), for sampling volatile organics from stationary sources, specifies the use of petroleum-base charcoal in the second sorbent tube. Charcoal has proven to be a marginal performer as a sampling sorbent, partly due to inconsistency in analyte recovery. In addition, commercial availability of petroleum charcoal for VOST tubes has been variable. Lack of data on comparability and variability of charcoals for VOST application has created uncertainty when other charcoals are substituted.

Five potential sorbent replacements for charcoal in Method 0030 were evaluated along with a reference charcoal. Two of the sorbents tested, Ambersorb XE-340 and Tenax GR, did not perform well enough to qualify as replacements. Three candidates, Anasorb 747, Carbosieve S-III and Kureha Beaded Activated Charcoal, performed adequately, and produced statistically equivalent results. Because Anasorb 747 exhibited an excellent combination of performance, availability, and cost, it was selected for use in field tests to follow this study.

INTRODUCTION

The Volatile Organic Sampling Train (VOST), EPA Method 0030, has been the method of choice for sampling most volatile organic compounds since its introduction (1,2). Fig. 1 is a schematic diagram of the VOST. Two of the key elements of the train are the two sorbent cartridges. These cartridges are the primary devices for collection and concentration of the volatile compounds in the flue gas being sampled. The front sorbent tube contains 1.6 g of Tenax-GC, a polymer of 2,6-diphenylene oxide, one of many porous polymer bead materials often used for sampling or for gas chromatography column packing. The VOST method was designed with the intent of capturing all of the compounds of interest on the front tube, with the back tube serving as a secondary trap in case of breakthrough of the more volatile compounds. In order to minimize potential breakthrough of the second tube, it contains 1.0 g of Tenax-GC, followed by 1.0 g of petroleum based charcoal.

The combination of Tenax-GC followed by charcoal is effective because the Tenax-GC traps all but the most volatile compounds and prevents them from being irreversibly sorbed by the charcoal. The charcoal, in turn, acts as a "safety net" and traps the few compounds which are not quantitatively sorbed by the Tenax-GC. It would be preferable to load both tubes with a single sorbent capable of quantitatively trapping all compounds of interest and exhibiting quantitative release of the compounds upon heat desorption. Unfortunately, no such ideal sorbent has yet been found and characterized.

Tenax-GC has served well as the primary sorbent in the VOST, and fortunately, most of the compounds of interest from incinerators are trapped on the front tube containing this material (3). The charcoal has performed adequately, but has been far from ideal in several respects. It has sometimes been contaminated with organic material which has been difficult to remove and which has complicated analysis and limited detection limits. In addition, charcoal has exhibited inconsistency of composition and uncertainty of supply.

Method 0030 specifies petroleum charcoal from SKC Lot 104 or equivalent, but gives no procedure for determining equivalency. Petroleum based charcoal was chosen because it is slightly hydrophobic and, therefore, does not retain water as readily as coconut charcoal and its sorption properties are not sensitive to the presence of water. Petroleum charcoal also shows less tendency than coconut charcoal to irreversible sorption of compounds sampled. Lot 104 charcoal became unavailable several years ago, and samplers have sometimes had difficulties obtaining petroleum charcoal in any form. Coconut charcoal has sometimes been substituted, with uncertain effect upon both sampling and analysis.

The goal of this project was to find and test a sorbent with sorption and recovery behavior at least as good as petroleum charcoal, with better consistency of properties and availability, and hopefully with lower contaminant levels and water sensitivity.

EXPERIMENTAL

The project was carried out in three experimental phases. Phase One was a screening study

designed to determine suitability of a series of sorbents for more extensive testing. Phase Two involved upgrading the stack sampling simulation, and showed the need for improvements in the sorbent spiking procedure and the analysis method. Phase Three included determination of optimum desorption temperature, development of an improved sorbent cleaning procedure, determination of the best calibration method, and dynamic spiking and recovery studies of a modified VOST. The dynamic spiking experiments of Phase Three will be described in detail, but only the conclusions of the other portions of that phase will be presented.

Phase One. Five sorbents were tested in the initial screening study. Petroleum based charcoal (SKC Lot 208) was chosen as the reference material to represent the original SKC Lot 104, which is no longer available. The other four sorbents tested were Ambersorb XE-340 (available from SKC), Anasorb 747 (SKC Lot 645), Carbosieve S-III (available from Supelco) and Tenax-GR (available from Alltech). Ambersorb XE-340 is a hydrophobic carbonized resin bead. Anasorb 747 is a beaded active carbon with a very regular pore size and structure which should contribute to consistent performance characteristics. Carbosieve S-III is a carbon molecular sieve which is widely used in conjunction with Carbopak sorbent in commercial analytical desorption traps. Tenax-GR, not to be confused with Tenax-GC, is a new material only recently made commercially available. Tenax-GR consists of Tenax with graphite incorporated into the particles. The intent of the manufacturer was apparently to produce a sorbent with the virtues of both constituents.

Twelve test compounds shown in Table I were selected to serve as a representative set of volatile organics spanning the practical limits of Method 0030. Three compounds were selected to serve as surrogates for all three phases, and are the first compounds listed in Table III. The Phase One analyte recovery and detection limit study utilized VOST tube pairs prepared as specified in Method 0030. The front tube was packed with 1.6 g of Tenax-GC and 1.0 g each of Tenax-GC and the candidate sorbent were loaded into the rear tube. Analytes and surrogates were loaded onto clean VOST tube pairs by a flash vaporization technique. The paired tubes were connected to a heated injection port so that the flow of high purity nitrogen carrier gas entered the front Tenax-GC tube and exited from the rear of the sequential sorbent tube. The target analytes (25 ng) and surrogates (250 ng) in methanol solution were then injected into the injection port with a microliter syringe. The carrier gas swept the volatilized compounds onto the sorbent tubes. The tube pair was placed in an ambient temperature purging apparatus, and was purged for 20 min with a total of 20 L of high purity nitrogen in order to simulate sampling conditions. Sample tubes were sealed and stored to await analysis.

Analysis of these compounds on the sample tubes prepared by the procedure described above, was performed using a slightly modified version of Method 5041 (4). Method 5041 includes heat desorption, purge and trap, and gas chromatography/ mass spectrometry. Readers interested in further details on the modifications made to Method 5041 and the reasons for them, are referred to the EPA report on this project (5). A detection limit study for the test analytes was performed for each sorbent. Each study was carried out according to instructions given in Reference 6. Seven replicate sets of tubes were analyzed for each candidate sorbent.

Phase Two. Phase Two of the project was designed to provide additional, more realistic testing for the candidate sorbents which survived Phase I. The VOST sample pairs were

prepared containing Tenax-GC in the front tube and only candidate sorbent in the rear tube. The paired tubes were cleaned, blank checked, and then spiked with relatively low levels of target compounds in a dynamic atmosphere generator to simulate the hot, wet conditions of a stack. The spiked VOST pairs were analyzed front and back separately to determine both recovery and distribution of target compounds.

A dynamic spiking apparatus was designed to simulate stationary source stack conditions as closely as possible. Ambient high-purity nitrogen carrier gas was admitted into the front of the system and then passed through a heated glass coil. Immediately after this gas pre-heating point, purified analyte-free water was admitted into the system at a constant rate metered by an HPLC pump. The gas-water mixture was then passed through a second heated glass coil to complete vaporization. After this second heating coil, target compounds were spiked into the system at a constant rate as metered by mass flow controllers. Bromochloromethane and chloroethane were added to the list of test compounds used in Phase One, bringing the total to fourteen for Phase Two. The target compounds were in a gaseous state and administered from a certified Scott cylinder. The moist, pollutant-laden stream then passed out of the dynamic spiking apparatus and into a standard VOST train. Tubes were spiked with 100 ng of each compound. As in Phase One, samples were analyzed by a slightly modified Method 5041.

Phase Three. A fifth sorbent was added to the four successful candidates from Phases One and Two. Kureha Beaded Activated Carbon (BAC) was obtained from Kureha Chemical Industry Co., Japan. BAC has been used for VOST testing with apparent success, and seems to be similar to Anasorb 747 in structure and performance. Phase Three included determination of the optimum desorption temperature, development of an improved sorbent cleaning procedure, determination of the best calibration method for the analytical system, and dynamic spiking and recovery studies of a modified VOST. Space only permits description of the dynamic spiking experiments, but conclusions of the other portions will be briefly presented in a later section. For complete experimental details of Phase Three, see Reference 5.

The triplicate dynamic spiking study was designed to provide a comprehensive picture of the performance characteristics of each of the candidate sorbents in realistic VOST applications. A new dynamic spiking apparatus was built and tested, and it was shown that VOST cartridges could be reproducibly spiked with various levels of analytes. A modified VOST configuration was adopted in order to give greater protection against breakthrough of the non-gaseous analytes which had displayed poor recovery from the candidate sorbents in the early phases of the project. This configuration consisted of front and middle tubes containing Tenax-GC, and a full tube of candidate sorbent in the back.

The dynamic spiking apparatus consisted of four major sections, a carrier gas moisturizing section, a spiking and primary mixing chamber, a secondary mixing chamber and a sampling manifold. The system operated at approximately 175°C and 11% moisture, in order to be consistent with a hot moist flue gas.

The dynamic spiking system was sampled using the three tube modified VOST, following procedures in Method 0030. Triplicate runs were conducted for each candidate sorbent at three spiking levels, approximately 100 ng, 200 ng, and 300 ng. These spike levels represent normal

levels encountered during actual field sampling with the VOST. Lower spike levels were used in Phase One because a detection limit study was an important part of the initial screening. Detection limit studies, because of their very nature, must be carried out at the lower end of the operating range. The expanded list of twenty three test compounds and three surrogates is shown in Table III. The VOST tubes collected 1L/min of sample for 20 minutes, giving a 20L sample. The tubes were then sealed, and either analyzed immediately or stored appropriately. Each three tube modified VOST functioned as a unit, but the tubes were analyzed separately in order to provide analyte distribution information. Analysis was by the modification of Method 5041 used in Phase One, except that carbonaceous sorbents and Tenax-GC were heat desorbed at 250°C.

RESULTS AND DISCUSSION

Phase One. As previously mentioned, seven replicate sets of tubes were analyzed in Phase One. Average values are used in this paper, but all data is included in Reference 4. Table I presents the detection limits determined by this study. Since detection limit as defined by the protocol used is a complex function of both sensitivity and reproducibility, it can serve as an important measure of the effectiveness of the sorbents being tested. In general, the lower the detection limit in Table I, the better the sorbent performed. Some caution must be exercised, however, in applying this principle. Although the 3 ng detection limit for vinyl chloride would ordinarily indicate excellent performance of Tenax-GR, it is accompanied, in this case, by an entirely unacceptable recovery of only 1% as shown in Table II. Three of the analytes, chloromethane, toluene, and methylene chloride produced unacceptable results that were probably not the fault of the sorbents, but contamination and other effects.

Table II shows the recoveries for the test analytes. The chloromethane, toluene, benzene and methylene chloride results were generally poor, and cannot generally be used for sorbent performance comparisons. For the remaining test compounds, all the candidate sorbents showed acceptable performance except that both Ambersorb XE-340 and Tenax-GR displayed low recovery of vinyl chloride. The very low recovery of chloromethane from Tenax-GR is the single instance in which the chloromethane data may be used, since it strongly indicates breakthrough of the low boiling compound.

Phase Two. Phase two results showed inconsistencies in the dynamic spiking system, and the need for improvements in the sorbent cleaning system and in the heat desorption of analytes from the carbonaceous sorbents. Considerable data was generated in Phase Two, and is presented in full in the project report.

Phase Three. Table III shows recoveries from the 200 ng spiking experiment. The values shown are averages of triplicate determinations. The coefficients of variation were generally better than 25%. A complete set of statistical tables is included in the project report, along with all raw data and analyte distribution information. The scope of this paper does not allow presentation of the very large data set generated. Identical spiking studies were carried out at analyte levels of 100 ng and 300 ng. The data produced show the same general patterns as those in Table III.

CONCLUSIONS

Phase One. Tenax-GR performed poorly with respect to recovery of low boilers, and was eliminated from the later phases of the project. Ambersorb XE-340 exhibited marginal performance for low boilers, but was carried forward, partly because of excellent performance with respect to the compounds in the middle range of boiling point applicability. The other candidates performed in a similar manner to each other and were carried forward to Phase Two.

Phase Two. Inconsistencies in Phase Two data showed the need for development and improvement in the dynamic spiking equipment and procedure, in the sorbent cleaning procedure, and in the analysis method.

Phase Three. This phase produced a number of important conclusions. Even though previous discussion only supports the conclusions related to the dynamic spiking experiments, several others are included for added perspective.

The carbon-based sorbents tested in this project showed strong adsorptive properties toward non-gaseous VOST analytes. These analytes could be recovered at only 50% or less, even at desorption temperatures of $350°C$. This means that it is still essential to include Tenax-GC ahead of the carbonaceous sorbents to prevent analyte loss. A thermal desorption temperature of $250°C$ was sufficient to desorb the light compounds from the candidate sorbent tubes. Higher temperatures gave no significantly increased recoveries.

Tenax-GC should be cleaned at $250°C$ for eight to twelve hours and carbon-based sorbents should be cleaned at $300°C$ for twelve to eighteen hours. All tubes should be purged with inert gas while being thermally cleaned.

A calibration curve with analytes and internal standards purged from water was superior to the other methods tested for initial calibrations and daily QC analyses.

VOST sample sets in the modified configuration could be accurately and reproducibly spiked with target analytes through the use of a dynamic spiking apparatus which simulated a stack environment.

A dynamic spiking study demonstrated that Ambersorb XE-340 performed very poorly for vinyl chloride and is not an acceptable replacement for charcoal in the VOST. A statistical evaluation of the sorbent recoveries confirmed that at a given dynamic spiking level, performance differences for the other three candidates and the reference charcoal measured in terms of percent recoveries of analytes were not significant. Based on performance alone, any of these three would be an acceptable replacement for charcoal in the VOST.

Because Anasorb 747 exhibited an excellent combination of performance, availability, and cost, it was selected for use in field tests of the three-tube VOST.

FURTHER WORK

Two other significant related projects have been completed and will be published in the near future. A draft three-tube VOST method using Anasorb 747 has been written, and is under review as an alternative to Method 0030. A field test in which the new VOST method was evaluated along with Method 0030 has been carried out.

NOTICE

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Table I

Analyte Detection Limits in Nanograms
Phase One Method Detection Limit Study

Target Compounds	Petroleum Charcoal	Ambersorb XE-340	Anasorb 747	Carbosieve S-III	Tenax-GR
Chloromethane	82	64	482	490	12
Chlorobenzene	8	16	9	10	32
Vinyl Chloride	5	26	10	9	3
1,1-Dichloroethene	16	17	6	14	52
Chloroform	10	5	6	9	43
Toluene	122	117	132	79	102
Methylene Chloride	35	306	77	386	46
1,1,1-Trichloroethane	6	14	13	39	44
Carbon Tetrachloride	7	10	15	33	43
Benzene	16	43	60	9	75
Trichloroethene	7	6	5	8	44
Tetrachloroethene	7	10	5	11	40

Table II

Average Percent Recoveries For Target Analytes
Phase One Method Detection Limit Study

Target Compounds	Petroleum Charcoal	Ambersorb XE-340	Anasorb 747	Carbosieve S-III	Tenax-GR
Chloromethane	247	164	1017	710	15
Chlorobenzene	80	76	76	79	87
Vinyl Chloride	87	47	94	77	2
1,1-Dichloroethene	102	90	101	87	99
Chloroform	102	100	88	92	102
Toluene	484	340	299	313	327
Methylene Chloride	176	389	215	491	222
1,1,1-Trichloroethane	101	114	98	120	104
Carbon Tetrachloride	102	109	88	105	100
Benzene	117	247	138	95	197
Trichloroethene	98	100	89	87	96
Tetrachloroethene	96	91	88	85	94

Table III

Average Percent Recoveries from Triplicate Sampling Runs
200 ng Spiking Level
Phase Three

|	Target Compound	Petroleum Charcoal	Anasorb 747	Ambersorb XE-340	Carbosieve S-III	Kureha BAC
1.	d4-1,2-Dichloroethane (Surr.)	NA	NA	NA	NA	NA
2.	d8-Toluene (Surr.)	NA	NA	NA	NA	NA
3.	p-Bromofluorobenzene (Surr.)	NA	NA	NA	NA	NA
4.	Chloromethane	4055	410	142	371	397
5.	Vinyl Chloride	65	87	3	82	74
6.	Bromomethane	61	38	42	54	22
7.	Chloroethane	52	49	59	49	38
8.	Trichlorofluoromethane	99	98	126	100	88
9.	1,1-Dichloroethene	80	84	72	77	80
10.	Methylene Chloride	97	101	106	96	94
11.	Iodomethane	70	69	64	57	61
12.	1,1-Dichloroethane	80	85	83	80	89
13.	Chloroform	78	80	81	77	85
14.	1,1,1-Trichloroethane	75	78	77	72	78
15.	Carbon Tetrachloride	71	74	70	63	76
16.	Benzene	87	96	147	84	94
17.	1,2-Dichloroethane	68	70	69	68	77
18.	Trichloroethene	87	90	85	86	97
19.	1,2-Dichloropropane	79	79	81	80	87
20.	cis-1,3-Dichloropropene	56	55	57	57	61
21.	Toluene	83	95	114	91	83
22.	trans-1,3-Dichloropropene	71	65	70	70	76
23.	1,1,2-Trichloroethane	23	80	85	84	90
24.	Tetrachloroethene	83	84	88	88	94
25.	n-Octane	115	104	108	104	93
26.	Chlorobenzene	79	78	77	81	88
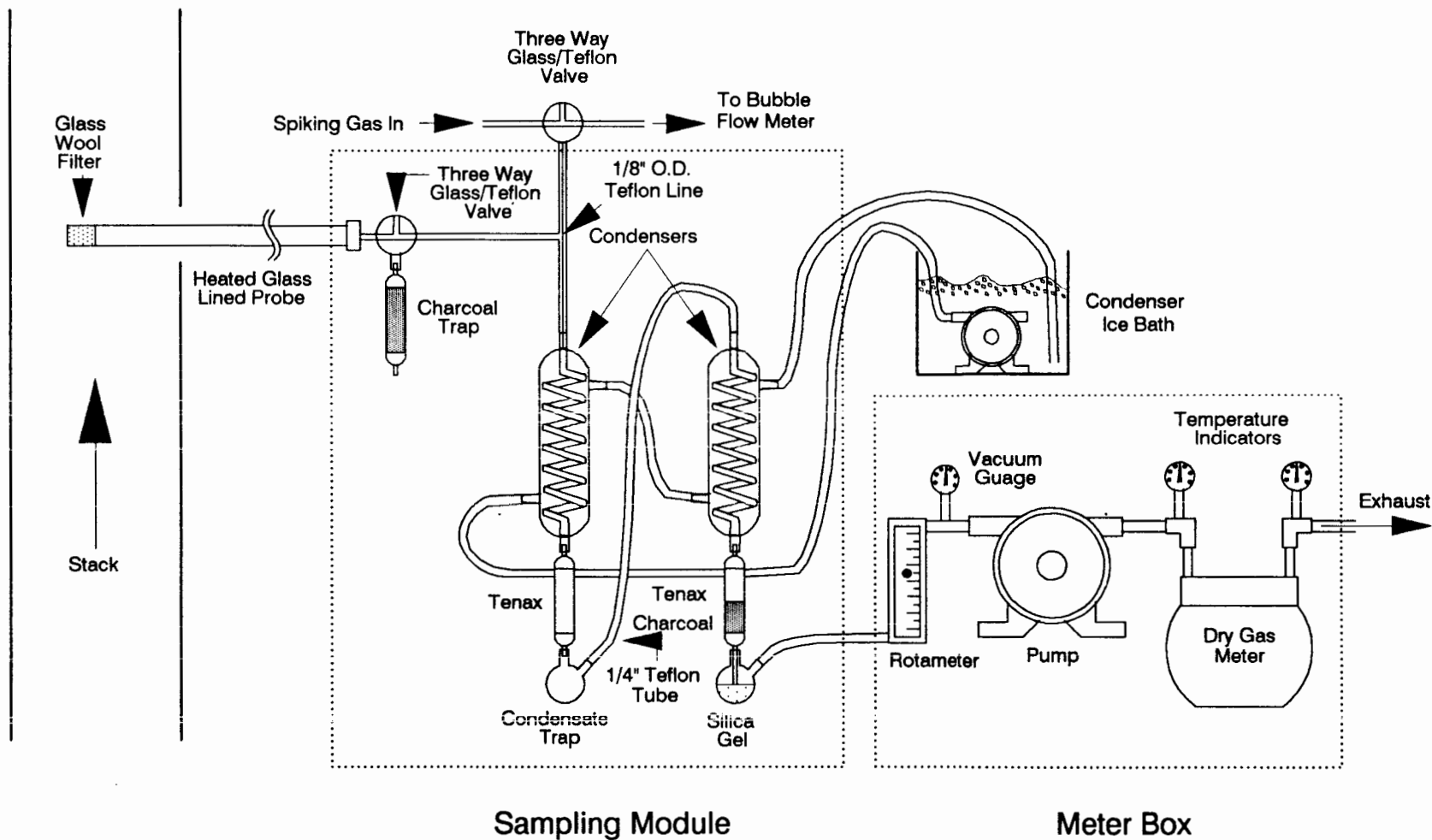
Figure 1. Volatile Organic Sampling Train